STUDIES OF CHLORDANE AVAILABILITY AND VOLATILITY IN AIR FORCE SOILS AND FACILITIES

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Background

Commercial chlordane, technical grade, is a mixture of more than 140 compounds, including the chlorocyclodiene compounds (Dearth and Hites 1991). The *cis*- and *trans*- isomers of chlordane make up 60-85% of the commercial mixture depending on the manufacturing process (Buchert et al. 1989). The use of chlordane in this report refers to both isomers. Commercial chlordane has been used worldwide as an effective insecticide but has been banned in the United States since the late 1980's and worldwide since 2004 due to its toxicity and persistence in the environment. Although banned for 20 years, chlordane is still being detected in soil and groundwater samples around the world (Sholtz and Bidleman 2007).

As bases are closed, contracted, or realigned, soil issues associated with this pesticide must be addressed including worker exposure and potential vapor intrusion resulting from rebuilding on contaminated soil. Several cases of temporary illness due to overexposure to chlordane in residences have been reported; however all reported cases appear to be due to inappropriate application of the pesticide (Callahan 1970, Olas et al. 1976, Vinopal and Olds 1977). An extensive survey of residences for indoor chlordane vapor concentration showed that most problems appear to be related to post-construction sub-slab injection of technical chlordane in building with ventilation ducts either in or below the foundation (Livingston et al. 1981, Lillie 1981 and 1982).

People are exposed to chlordane through ingestion, dermal exposure, or inhalation of vapors. Chlordane primarily affects the nervous system and the digestive system causing headaches, irritability, confusion and vision problems as well as vomiting, stomach cramps and jaundice (ATSDR 1994). The EPA has set a drinking water limit of 2 ppb. The Food and Drug Administration (FDA) limits chlordane in fruits and vegetables to <300 ppb, and <100 ppb in animal fat and fish (ATSDR 1994). Exposure in the workplace environment is limited to 0.5 mg chlordane/m^3 in an 8-hr workday (NIOSH 2005).

Chlordane is highly hydrophobic and binds strongly to organic carbon, clay and silt in anaerobic sediments (Nakano et al. 2004). Chlordane in surface soil undergoes a two-step desorption process. The initial "fast" desorption results in volatilization into the atmosphere (Meijer et al. 2003a). Scholtz and Bidleman (2007) have prepared a long-term predictive model of the fate of chlordane isomers in soil. The model predicts that chlordane is immobile in soil. Field data, which supports this prediction, has determined that leaching is not a transport mechanism for chlordane. However, volatilization is an important route of loss of soil residues. The rate limiting factor is soil binding not atmospheric concentration.

Chlordane undergoes photodegradation in the environment and UV irradiation has been applied experimentally to remediate contaminated groundwater. The irradiation has been combined with H_2/NaOH and 2-propanol (Kitchens et al. 1984), water or ethanol (Buser and Miller 1993, Yamada et al. 2008). Several case studies on chemical remediation of chlordane to treat soil/sediment have been reported on the website of the Federal Remediation Technology Roundtable (FRTR) (2008). Two of the sites employed thermal desorption of the pesticide. The FCX Superfund Site in Washington State met a cleanup goal of total pesticide equal to 1 mg/kg, and the Arlington Blending and Packaging Superfund Site met a cleanup goal for chlordane of 3.3 mg/kg. The Parsons Chemical/ETM Enterprises Superfund Site, involved vitrification of the contaminated soil and met the cleanup goal for chlordane of 1 mg/kg at 25 lbs soil /hour. Other research has reported on chemical remediation of related pesticides, the hexachlorocyclohexanes (HCH) and various aldicarb species including Temik, and

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Form Approved
OMB No. 0704-0188

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1. REPORT DATE **MAR 2011**	2. REPORT TYPE	3. DATES COVERED **00-00-2011 to 00-00-2011**
4. TITLE AND SUBTITLE **Studies of Chlordane Availability and Volatility in Air Force Soils and Facilities**		5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)		5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **U.S. Army Engineer Research and Development Center (ERDC),3909 Halls Ferry Road,Vicksburg,MS,39180**		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
Presented at the 2011 Air Force Restoration and Technology Transfer Workshop "Collaboration for Closure", 7 - 11 March 2011, San Antonio, Texas

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**4**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

diuron, in aqueous systems. Ngabe et al. (1993) used base hydrolysis to remove HCH in a system simulating cold, deep lake or ocean water. Miles and Delfino (1985) studied base hydrolysis of aldicarb in groundwater.

Because the organochlorine pesticides exist in an oxidized state, they are generally not amenable to aerobic oxidation processes, except in the case of co-metabolism. Therefore, research has been directed toward anaerobic reduction processes. Hydrogen Release Compound (HRC) has been studied for many years as an amendment to encourage biological remediation of groundwater, including chlordane (Fennell et al. 2003). Groundwater has also been treated at the Ft. Pierce, FL, Orkin facility with hydrogen peroxide and nutrients to stimulate biodegradation of chlordane (FRTR 2008). Phytoremediation of a related pesticide, dieldrin, concluded that, while not biodegraded, uptake of dieldrin into the roots of poplar and willow trees was a potentially useful tool for removing the pesticide from groundwater (Skaates et al. 2005). The potential of fungi to aerobically degrade/transform alkyl halides such as chlordane has been explored using *Phanerochaete chrysosporium*, the white rot fungus, and reviewed by Gadd (2004). In one study, approximately 23% of chlordane was mineralized in 30 days in liquid culture and 60 days in solid culture (Kennedy et al. 1990). Anaerobic biodegradation however, has been reported to produce chlorobenzenes and polymerization to α-hexachlorocyclohexane in some related pesticides (Benezet and Matsumura 1973).

Materials and Methods

Laboratory tests were conducted on soils from Air Force facilities with aged chlordane contamination to estimate the bioavailability of the contaminant. Soils were tested from McGuire AFB in New Jersey with moderate chlordane contamination levels (1,100-5,500 ppb) and Davis-Monthan AFB in Arizona with significantly higher contamination levels (4,300-20,100 ppb). Tests were conducted on *Lumbricus terrestris*, earthworms, to estimate availability and effects on terrestrial invertebrates. Tests were also conducted on two common grasses, Kentucky Bluegrass (*Poa pratensis*) and Perennial Ryegrass (*Lolium perenne*) and one sedge, Yellow Nutsedge (*Cyperus esculentus*). Three different leaching tests were conducted to estimate aged chlordanes aqueous mobility in surface soil, Synthetic Precipitation Leaching Procedure (SPLP), landfill environment, Toxicity Characteristic Leaching Procedure (TCLP), and in the human digestive tract, Physiologically Based Extraction Test (PBET).

Treatability tests were conducted to estimate the potential effectiveness of easy to apply chemical treatments. First base hydrolysis with hydrated lime was attempted on an aqueous solution followed by treatment of soil slurry. Heat-activated persulfate treatment of the soil in a slurry was also attempted. Biotreatment of the soil by composting with a spent mushroom substrate was also conducted.

Laboratory and field tests were also conducted to estimate rates volatilization under controlled laboratory and field conditions using the same soils as the bioavailability and treatability tests. Laboratory tests investigated the effects of temperature, humidity and soil disturbance chlordane volatilization from the McGuire and Davis-Monthan AFB soils. These tests were used to estimate flux rates of chlordane from aged soil. Field tests at Ft. Dix Army Base investigated the potential for overexposure to chlordane by construction workers on contaminated sites. Field tests at Mountain Home AFB investigated vapor intrusion into slab-on-grade dwellings. Tests for construction worker exposure collected vapor from a 2-inch bore hole to simulate a relatively confined excavation and flux chambers to estimate exposure from unconfined surface work such as grading. Vapor intrusion tests included collection of indoor air, sub-slab air, and associated sub-slab soil samples at eight different dwellings.

Results and Discussion

Uptake and tests on bioavailability to earthworms indicated that aged chlordane in soils did not significantly impact mortality but did severely impact reproduction. In the higher contaminated soil from Davis-Monthan AFB, earthworm avoidance was evident as well complete cessation of earthworm reproduction. Tests with the grasses and sedge showed that chlordane contamination did not affect the rate of seed germination, but chlordane uptake into the roots and translocation to the shoots was seen in all plants.

Analytical results of extracts from tests for chlordane aqueous mobility in surface soils (SPLP), landfill environments (TCLP), and human digestive tract (PBET) were all non-detect. This is an indication that leaching of chlordane from soils under common conditions is not likely. Likewise chemical treatment tests of chlordane contaminated soils in slurries showed no significant loss of chlordane.

Laboratory tests of chlordane volatility indicated that high relative humidity (RH) and temperatures can significantly increase the flux rate of chlordane from the test soils. Flux rates of 9.0 $\mu g\ m^{-2}\ day^{-1}$ at 50° C (50% RH) and 14.2 $\mu g\ m^{-2}\ day^{-1}$ at 90% RH (22° C) were measured in the McGuire AFB soil. A flux rate of 41.8 $\mu g\ m^{-2}\ day^{-1}$ (22° C, 50% RH) was measured in the Davis-Monthan AFB soil having much higher contamination levels. Estimations of building air exchange rates necessary to produce a target indoor air concentration for a 10^{-6} cancer

risk were calculated using the calculated flux rates from these tests and standard assumptions found in the Johnson and Ettinger (J&E) model for subsurface foundation area, building volume, and crack width,. These calculations indicated that building air exchange rates would need to be one to two orders of magnitude lower than the conservative estimate used in the J&E model. Incorporation of flux rates into the J&E model could potentially show that many compounds currently included as potential candidates for vapor are not threats under most situations.

Field tests at Ft. Dix Army base indicated that semi-confined excavation may pose some short term exposure to chlordane vapor, but values were far below OSHA workplace exposure standards. Shallow unconfined soil disturbances did not produce any detectable levels of chlordane vapor. Exposure to chlordane vapor should not be an issue for construction activities.

Field tests at Mt. Home AFB did not produce any detectable results for chlordane. Information from subsequent sampling prior to demolition activity at the site indicated that the sites were treated with dieldrin instead of chlordane. Reanalysis of chromatograms showed dieldrin was present in many of the samples. Dieldrin results did not show any correlation between soil concentrations and sub-slab gas concentrations; however results did show that the J&E model over predicts sub-slab gas concentrations from soil concentrations in most cases at this site. This work also revealed that current sample collections techniques for sub-slab gas samples are not adequate to reach needed detection levels. These methods require extremely large sample volumes, which are likely to draw air from outside the foundation and require very lengthy sample durations. A passive sampling technique should be developed for sub-slab sampling of these contaminants if they remain on the potential vapor intrusion list.

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